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Review

Dry fractionation process as an important step in current and future lignocellulose biorefineries: A review

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HIGHLIGHTS

- ▶ The choice of pretreatment depends on the heterogeneity of lignocellulosic materials.
- ▶ The breakdown of lignocelluloses is a necessary step within biofuel production processes.
- ▶ Currently, mechanical size reduction steps are not cost-effective.
- ▶ The factors influence the performances of biomass mechanical treatment is discussed.
- ▶ Innovative grinding processes or combinations with others pretreatments are required.

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ABSTRACT

The use of lignocellulosic biomass is promising for biofuels and materials and new technologies for the conversion need to be developed. However, the inherent properties of native lignocellulosic materials make them resistant to enzymatic and chemical degradation. Lignocellulosic biomass requires being pretreated to change the physical and chemical properties of lignocellulosic matrix in order to increase cell wall polymers accessibility and bioavailability. Mechanical size reduction may be chemical free intensive operation thanks to decreasing particles size and cellulose crystallinity, and increasing accessible surface area. Changes in these parameters improve the digestibility and the bioconversion of lignocellulosic biomass. However, mechanical size reduction requires cost-effective approaches from an energy input point of view. Therefore, the energy consumption in relation to physicochemical properties of lignocellulosic biomass was discussed. Even more, chemical treatments combined with physicochemical size reduction approaches are proposed to reduce energy consumption in this review.

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1. Introduction

Renewable lignocellulosic biomass, as a promising alternative to limited crude oil, can be utilized to produce biofuels, biomolecules and biomaterials (Fig. 1). Lignocellulosic biomass "plant cell walls" consist mainly of cellulose, hemicellulose and lignin. These polymers, together with small amounts of other components, like acetyl groups, minerals and phenolic substituents, are organized in complex non-uniform three-dimensional structures; these are only partly described for different plants (Fry, 1986; McNeil et al., 1975; Salmen and Olsson, 1998). Also the utilization of cell wall components through enzymatic and chemical conversions is depending on various plant fractions as well as on the different development stages and different types of cell walls. The interactions into extensive and complex molecular and macromolecular networks between the cellulosic, hemicellulosic, and lignin fractions within the cell wall matrix are thought to be the reason for the differences in reactivity. Information about the composition and organization of plant cell walls, under a wide range of growth conditions, is of vital importance to understand and develop targeted procedures for mechanical, chemical and biological degradation and optimized utilization of lignocellulosic materials (Fig. 1). The production of biofuels from lignocellulosic biomass by biological degradation is one of the routes that can contribute to a future sustainable bio based society; the challenge is to find the appropriate microorganisms and enzymes that can convert hemicelluloses and cellulose into bioenergy (Brethauer and Wyman, 2010; Kaparaju et al., 2009). However, the inherent properties and the composite structure of native lignocellulosic materials make them resistant to enzymatic action. The crystallinity of cellulose and structure of hemicelluloses, their accessible surface area, protection by lignin, and cellulose–hemicelluloses–lignin association are the main factors affecting the rate of accessibility and digestibility (Fig. 2 and Table 1). These factors are the cause for the very slow biodegradation of native lignocelluloses and the often low ex-

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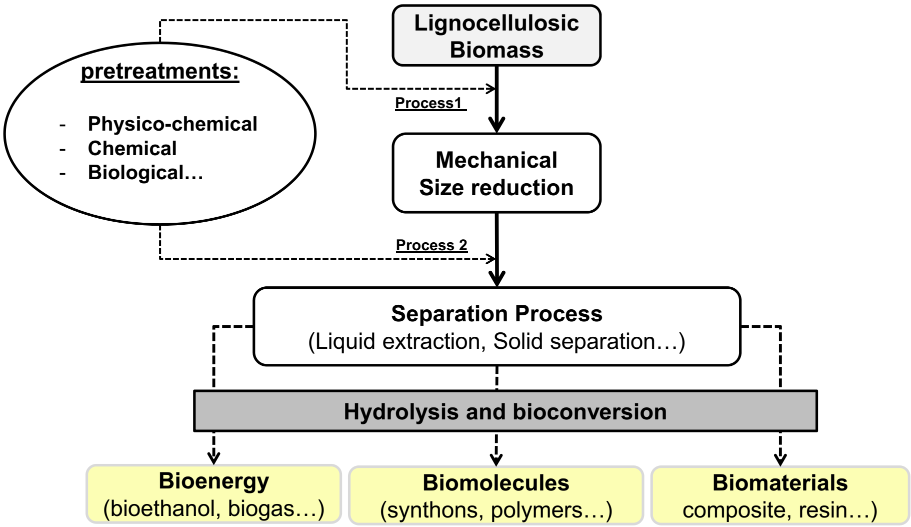
Lignocellulosic Biomass
pretreatments:
- Physico-chemical
- Chemical
- Biological…
Process1
Mechanical Size reduction
Process 2
Separation Process (Liquid extraction, Solid separation…)
Hydrolysis and bioconversion
Bioenergy (bioethanol, biogas…)
Biomolecules (synthons, polymers…)
Biomaterials composite, resin…)

Fig. 1. Simplified scheme for lignocellulose biorefineries processes.

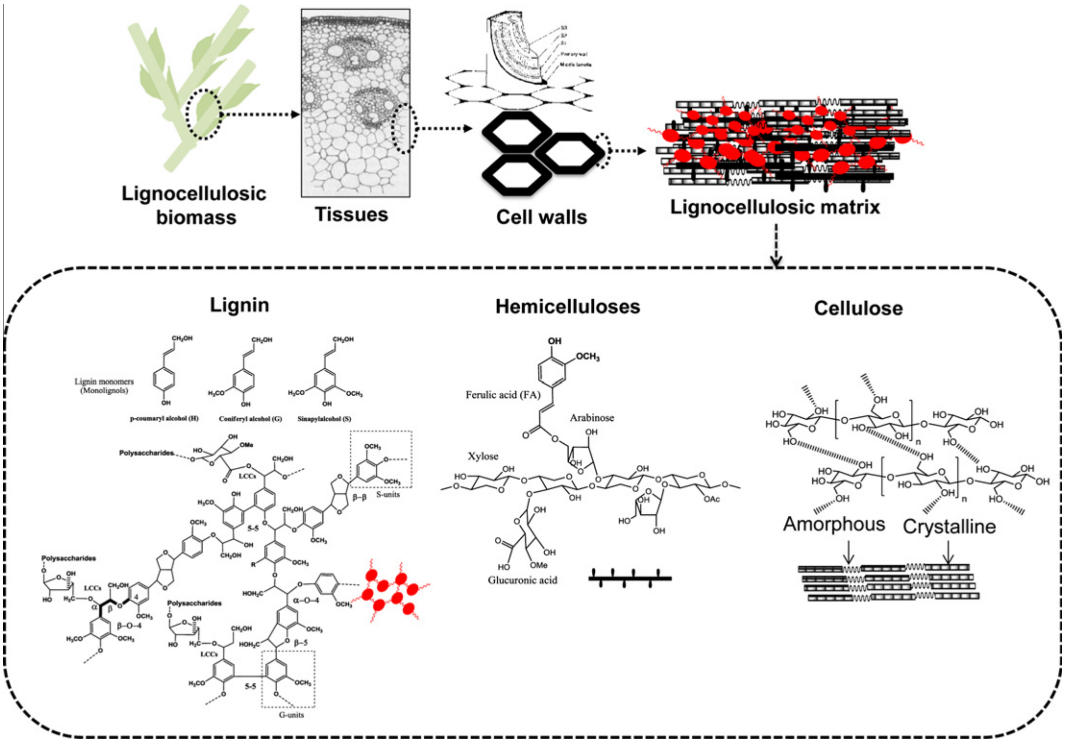

Fig. 2. Composition, structure and organization of lignocellulosic biomass.

tent of degradation which does not exceed 40%. Hence, the pretreatment of lignocellulosic biomass prior to biochemical attack is an essential step in order to increase cellulose and hemicelluloses accessibility and biodegradability. Application of pretreatment steps allows modifying the supramolecular structure of cellulose–hemicellulose–lignin matrix, thereby changing the natural binding characteristics of lignocellulosic materials and increasing the holocelluloses accessibility for enzymatic or chemical biological action (Fig. 1). A large number of pretreatment methods have been developed thus far (Kumar et al., 2009; Kumar and Wyman, 2009; Lee et al., 2007; Mosier et al., 2005; Taherzadeh and Karimi, 2008; Yang and Wyman, 2008; Zhu et al., 2008). Some chemical, physicochemical, biological, physical and mechanical pretreatments are known to be effective; however, these methods have some disadvantages in terms of energy consumption, corrosion of processing tools, introduction of inhibiting effects, the number of separation and purification steps, etc. To overcome the limitations of the individual operations, pretreatments can be conducted by combining mechanical size reduction with moderate chemical or physicochemical co-treatments. This combined "mild" preparation procedure reduces energy consumption, maintains cellulose polymer structures, and increases enzymatic accessibil-

Table 1
Biochemical composition and physicochemical properties of different lignocellulosic biomasses.

Lignocellulosic biomasses	Grasses and energetic plants						Hardwood		Softwood	
	Wheat straw	Wheat bran	Corn stover	Rice straw	Switchgrass	Miscanthus	Poplar	Eucalyptus	Spruce	Pine
Celluloses (%)	39.6	42.5	38.8	32.0	40.1	37.7	44.5	54.1	45.5	43.3
CrI	50.3	n.d.	50.3	51.7		n.d.	49.9	54.3	38.4	n.d.
Hemicelluloses (%)	26.6	21.2	29.6	18.0	25.6	37.3	22.5	18.4	22.9	21.5
Xylose (Xyl)	24.3	15.4	22.2	14.3	22.1	33.8	19.4	15.0	6.6	5.3
Arabinose (Ara)	2.1	3.1	5.5	2.3	2.5	2.8	0.5	0.5	1.2	1.6
Galactose	0.2	2.7	2.9	1.2	1.0	0.6	2.0	1.5	0.6	2.9
Mannose	–	–	–	0.2	nd	0.1	0.6	1.5	13.5	10.7
Ara/Xyl	0.09	0.20	0.25	0.16	nd	0.08	0.025	0.03	0.18	0.3
Lignin (%)	21.0	3.4	22.1	11.2	18.8	25.1	19.5	21.5	27.9	28.3
G/S/H	49/46/05	–	35/61/4	45/60/15	–	–	41/59/nd	38/62/nd	98/tr/2	82/tr/18
β-O-4 (μmol/g of lignin)	1040	–	610	630	–	–	2390	2780	1230	1140

G: guaiacyl units in lignin; S: syringyl units; H: p-hydroxyphenyl; *CrI*: crystallinity index; nd: not detected; tr: traces.

ity. The environmentally friendly pretreatment procedures have been studied in detail focusing on milling, extrusion processes and thermal treatments; those do not require the use of specific acidic chemicals (Adapa et al., 2010; Da Silva et al., 2010; Hideno et al., 2009; Lee et al., 2009). The current use of chemicals is in part responsible for the expensive pretreatment steps in lignocellulose biorefineries; significant improvements are therefore imperative. The breakdown of lignocelluloses is a necessary step within biofuel production processes (Fig. 1). Mechanical pretreatments allow resulting in an improved conversion of saccharides during hydrolysis and improved total digestibility. For example, studies have shown that particles sizes must be reduced to 0.5–2 mm in order to decrease heat and mass transfer limitations and to reach a well-accepted level of digestibility. Currently, mechanical size reduction steps are not cost-effective because of too high energy demands of dry grinding operations; therefore, innovative grinding and milling processes or combinations of mechanical size reduction with others pretreatments are required. In this review, we address important aspects of pretreatment procedures in lignocellulose bio-refinery. First of all, we outline the heterogeneity of lignocellulosic materials and the difficulties in lignocellulosic biomass pretreatment for saccharification. In a second part, we present several mechanical size reduction methods for biofuel technology. Then, lignocellulose mechanical size reduction is described in more details and its influence on the previously mentioned parameters are discussed. We emphasize on both maximizing saccharification yield and energy efficiency of pretreatment procedures. Finally, we discuss the factors which can influence the performances of mechanical size reduction of lignocellulosic biomass and energy efficiency.

2. Molecular composition and organization of lignocellulosic plant cell wall

The plant cell develops its wall as a series of layers. The earliest-formed layer found at the center of the double wall formed by two adjacent cells corresponds to the middle lamella. Then the primary cell wall is deposited, which is followed by the formation of a secondary wall. Primary and secondary cell wall layers consist of two phases: a microfibrillar phase and a matrix phase (Fig. 2). The microfibrillar phase of the wall is composed of extremely long, tiny structures called microfibrils which are made up of cellulose. The cellulose chains are forming a crystalline or paracrystalline lattice within the microfibril. The non-crystalline phase of the cell wall (matrix) is composed of a variety of polysaccharides, proteins and phenolic compounds, which are chemically and physically interconnected within the tri-dimensional cell wall structure. Cell walls vary widely with the cell origins and cell types, in both the composition and heterogeneity, and this leads to different performances and properties. Previous studies have shown that the composition and structure of the cell wall differ within specific tissue (epidermal, parenchymatous, sclerenchyma and vessel tissues, etc.) and cell types in relation to growth and development (Sun et al., 2010) and that the plant cell wall components are not uniformly distributed within the cell walls. The structure and the quantity of cellulose, hemicellulose and lignin vary according to species, tissues and maturity of the plant cell wall (Table 1). Cellulose polymers consist of D-glucose subunits, linked by β-(1→4) glycosidic bonds (Fig. 2). The Hemicelluloses are branched polymers with short lateral chains built up of different sugar monomers which are present in almost all plant cell walls along with cellulose. Hemicelluloses serve as a connection between the lignin and the cellulose fibers and give cohesion to the whole cellulose–hemicellulose–lignin network (Fry, 1986; Salmen and Olsson, 1998; Watanabe, 1989). In general, the dominant hemicelluloses from all plant cell walls are xylans which display significant variability in their structural characteristics (Ebringerová and Heinze, 2000; Puls, 1997) (Table 1 and Fig. 2). Lignin is an amorphous heteropolymer consisting of the assembly of three different phenylpropane alcohols: p-coumaryl (H), coniferyl (G) and sinapyl (S) residues (Sarkanen and Hergert, 1971; Vanholme et al., 2008) (Fig. 2). The nature and the quantity of lignin monomers (H, G, S) vary according to species, tissues, maturity and the spatial localization in the cell (Table 1). The lignins from softwoods contain mainly guaïacyl units, those from hardwoods and grass mainly guaïacyl (G) and syringyl (S) units (Lapierre, 1993).

3. Factors limiting the bioconversion of lignocellulosic materials

The conversion of lignocellulosic materials is dependent not only on their biochemical composition but also on the organization of their constituents and the interaction between them. Biological, chemical and physicochemical conversion of lignocellulosic materials are affected by factors such as the crystallinity of the cellulose, the structure of hemicelluloses, structural surface area and pore volume, lignin composition, content and cross linking (Monlau et al., 2012a; Taherzadeh and Karimi, 2008; Zhu et al., 2008), all of which depend on the species, tissues, plant part, and plant maturity. All these parameters have been shown to influence the enzymatic accessibility and hydrolysis of holocelluloses in lignocellulosic plant cell wall (Chang and Holtzapple, 2000; Zhu et al., 2008). Some studies have shown a good correlation between crystallinity, surface properties, supramolecular structure and the rate of enzymatic hydrolysis of pure cellulose (Ciolacu et al., 2008; Gama and Mota, 1997; Mansfield and Meder, 2003). However, with lignocellulosic materials this relationship is not so evident, due to the more heterogeneous nature of this material and the contribution of other components such as lignin and hemicelluloses. Some works have reported that lignin polymer is the most recalcitrant component of the plant cell wall, and the higher the proportion of aromatics compounds, the higher the resistance to chemical and biological degradation (Akin, 2008; Hendriks and Zeeman, 2009; Zhu et al., 2008; Monlau et al., 2012b). The importance of removing lignin has been frequently suggested, because a correlation has been observed between delignification and increased sugar release (Chang and Holtzapple, 2000; Yang and Wyman, 2008). However, Rollin et al. (2010) reported that increasing cellulose accessibility was a more important factor than delignification for effectively releasing sugars from recalcitrant lignocellulose at high yield. On the other hand, Zhu et al. (2008) reported that lignin content and biomass crystallinity dominated digestibility, but at short hydrolysis periods, lignin content was not important for digestibility when crystallinity was low. Similarly, at long hydrolysis periods, crystallinity was not important to digestibility when lignin content was low. But cellulose crystallinity has been frequently suggested as of importance, because many studies have shown a correlation between crystallinity and yield in sugar release (Gupta and Lee, 2009; Yoshida et al., 2008). However, Da Silva et al. (2010) reported that sugar yield after wet disk milling increased independently of crystallinity decrease. Indeed, they have suggested that the number of operation cycles, resulting in reduction of particles size and fiber thickness, was the relevant factor in the improvement of enzymatic digestibility of the pretreated materials. Other studies have reported conflicting results with regard to the effect of accessible surface area on biomass digestibility. Fan et al. (1981) concluded that surface area had no effect on the digestibility of biomass. In contrast, Gharpuray et al. (1983) and Sinitsyn et al. (1991) determined that specific surface area played a major role in biomass enzymatic hydrolysis. Others authors suggested that the decrease of cellulose degradation occurs as a result of structural transformations during pretreatments and the initial stages of hydrolysis with the result that the more resistant fraction remains inaccessible (Gupta and Lee, 2009; Mansfield and Meder, 2003; Mooney et al., 1999). Lee et al. (2010a), suggested that during pretreatment the removal of hemicellulose and lignin from cell wall supramolecular structure create nanospace between cellulose microfibrils. This morphological characteristic and supramolecular structure improved the enzymatic saccharification yield. These summary results are contradictory, due to the very heterogeneous nature and complexity of lignocellulosic materials. In addition, enzymatic degradation of lignocellulose is still poorly understood because of contrasting effects between physicochemical properties of the substrate, synergies and/or competition between enzymatic pathways, and mass transfer phenomena. The aim of pretreatments is to modify materiel particle size, surface area and porosity, crystallinity of cellulose, lignin content and distribution in order to prepare the cellulose and hemicelluloses for enzymatic hydrolysis. The pretreatment of biomass is an essential step in order to increase carbohydrates, accessibility, and bioavailability and hydrolysis affectivity. The objective of pretreatments depends on the process type and biomass structure. For a biofuels process, the aim of a pretreatment is to change the lignocellulosic matrix properties in order to make the holocelluloses more accessible to enzymes or chemical attack (Monlau et al., 2012a; Kumar and Wyman, 2009). An effective and economical pretreatment increases the accessibility to carbohydrates without formation of inhibitors (Barakat et al., 2012; Palmqvist and Hahn-Hägerdal, 2000). In addition, the process should be inexpensive, low energy-demanding, and not causing any pollution (Table 1). Pretreatment methods can be divided into different categories: mechanical, chemical, physicochemical and biological or various combinations of these. In this review we focus on targeted mechanical size reduction schemes as an important step in lignocellulosic biomass pretreatment.

4. Mechanical size reduction

In the field of renewable energy from renewable biomass-based resources, mechanical size reduction is crucial for the densification process, an important step in transformation of feedstock into bioenergy (Schell and Harwood, 1994; Zhu et al., 2010a; Sharma et al., 1988; Silva and Rouau, 2011). Lignocellulosic biomass can be comminuted by combination of chipping, grinding, and milling. Such mechanical treatments lead to a reduction in the particle sizes; the following options exist: “powdering” (m to cm), coarse milling (cm to mm), and intermediate micronization (cm to 100 μm), and fine grinding (<100 μm) & ultra-fine grinding (<30 μm). Fractionation of lignocellulose into its three major components cellulose, hemicelluloses and lignin, constitutes an important goal of its refining. Achieving high fractionation yields and maintaining the integrity of the macromolecular fractionation products are of major importance regarding the effectiveness of the refining process.

Biomass size reduction is a mechanical treatment process which leads to rupture of plant cell wall and dissociation of tissues (epidermal, parenchymatous and vessel tissue). Mechanical pretreatment allows separating the main botanical parts of the crop into different fractions, to be used as feedstock for various applications. For example, wheat straw was refined into fibers, hemicellulosic sugars and lignin oligomers by means of a multi-stage fractionation treatment: mechanical separation of the plant components followed by one or two stage chemical fractionation processes (Papatheofanous et al., 1998). Yellow winter wheat straw was separated into two fractions by milling in a disc Mill: (a) chips, containing mostly internodes and (b) meal, consisting mainly of ground leaves and nodes (Papatheofanous et al., 1998). They concluded that the mechanical dissociation and separation of the botanical components using disc milling was rather efficient, i.e., all internodes passed in the chip fraction. The internode fraction (63% of the whole straw) contained 8% more cellulose, 9% more lignin and 10% less ash compared to the unfractionated material. Papatheofanous et al. (1998) reported that disc mill fractionation was particularly effective with respect to the separation of the non-lignocellulosic components, i.e., protein, extractives, etc. Fractionation of fibrous fraction from steam-exploded rice straw (SERS) of high moisture content have been studied with respect to the separation degree of fibrous tissue versus non-fibrous tissue including epidermal, parenchymatous and vessel tissues using a fluidized bed opposed jet mill (Jin and Chen, 2006, 2007). Chemical composition and fiber characteristics, such as fiber size and composed cell proportion were studied for the separated fibrous fraction of SERS. 70.4% high cellulose fibrous fraction with 63.1% fiber cell content and 65.6% cellulose content was produced from the fractionation process. Palmowski and Muller (2003) have also studied the effect of comminution on different organic samples (apples, rice, sunflower seeds, hay and maple leaves). After breakdown of these substrates, a release of soluble organic compounds occurred for two reasons: cells were destroyed through comminution and/or dissolution of organic components took place through newly-generated accessible surfaces. Size reduction of lignocellulosic biomass is also necessary to: (i) decrease cellulose crystallinity (*CrI*), (ii) increase total accessible specific surface area (*SSA*) and (iii) increase pore size of particles and the number of contact points for inter-particle bonding in the compaction process and (iv) reduce mass and heat transfer limitations during the hydrolysis reactions (Schell and Harwood, 1994). All these parameters improve the digestibility and the conversion of saccharides during hydrolysis (Monlau et al., 2012b; Palmowski and Muller, 2000; Zhu et al., 2008). Gharpuray et al. (1983) investigated the effects of ball milling, and roller milling on the structural features (crystallinity, surface area and lignin content) of wheat straw. Ball milling pretreatment was found to be effective in increasing the *SSA* (2.3 m^2/g compared to 0.64 m^2/g for the raw wheat straw) and decreasing the *CrI* (23.7 compared to 69.6 for the raw wheat straw). Also, Piccolo et al. (2010), reported that the *SSA* of wheat straw increased with more than 60% from the ball-milling treatment for 4 h compared to untreated and steam exploded material. They found that a more severe steam explosion treatment (0.2% w/w H_2SO_4 at 210 °C for 10 min) increased *SSA* of wheat straw from 1.9 to 3.1 m^2/g. Miao et al. (2011) investigated the mechanical size reduction of miscanthus and switchgrass using a commercial hammer mill and the resulting *SSA* measured using the geometry and density of particles. This method yielded accessible surface areas of 20.4 and 20.5 m^2/g when a hammer mill was used to grind miscanthus and switchgrass, respectively, with a screen size of 1 mm. The *CrI* of cellulose has been considered as an important factor in resisting enzymatic degradation. It has been suggested that the more accessible (amorphous) region (Fig. 2) of cellulose degrades more easily than the less accessible crystalline regions. In comparison, ball-milling for 10, 20 and 40 min of eucalyptus decreased the *CrI* from 59 to 26, 8% and 3%, respectively. In contrast, hydrothermolysis for 30 min at 160 °C increased the *CrI* from 59% to 68%, while organosolve treatment (50% EtOH + 1% AcOH) at 200 °C for 60 min decreased the *CrI* of eucalyptus to 48%. Mechanical size reduction is an important intensive unit operation essential for biological and chemical conversion processes. For hydrothermal conversion, pyrolysis, biochemical hydrolysis and fermentation, the goal of mechanical size reduction is to produce identical elongated particles with a large surface area and amorphous cellulose to be exposed to enzymes or chemical catalytic (Kumar et al., 2009; Mani et al., 2006). The finer the identical elongated particles, the larger specific particle area and amorphous cellulose, and the higher the bioconversion efficiency. However, mechanical size reduction may not be a cost-effective process because it requires a lot of energy. The literature reported that the energy requirement in relation to the final particle size is one of the most important economical parameters (Adapa et al., 2010; Kratky and Jirout, 2011; Mani et al., 2004; Miao et al., 2011; Zhu et al., 2009).

5. Factors affecting performance and energy consumption of mechanical size reduction processes

5.1. Biomass structure and properties (moisture content, chemical composition, etc.)

Lignocellulose properties and moisture content are also important factors to be considered during milling treatment of biomass (Table 2). From data presented in Table 2, it can be concluded that grinding energy decreased greatly as the moisture content was reduced. For example, Mani et al. (2004) reported that the specific energy requirement (*SER*) for grinding 7.7 mm wheat straw with 12% moisture content with a hammer mill using screen sizes of 0.8, 1.6 and 3.2 mm were 45.3, 43.6 and 24.7 kW h t^{-1}, respectively, (Table 2). The *SER* to reduce corn stover with moisture content of 12% from a particle size of 7.2 mm to pass a screen of 0.8, 1.6 and 3.2 mm were 34.3, 19.8 and 11.04 kW h t^{-1}, respectively, (Mani et al., 2004). However, Cadoche and Lopez (1989) reported a *SER* of 7.5 and 42.0 kW h t^{-1}, when a hammer and knife mills, respectively, was used to grind wheat straw with a screen size of 1.6 mm. A study of grinding switchgrass at 8% moisture content in a hammer mill was reported by Mani et al. (2004). They are reported that the *SER* was 51.8 kW h t^{-1} to reduce switchgrass from 7.2 to 1.6 mm. Miao et al. (2011) compared the *SER* to grind switchgrass and miscanthus using knife mill at 7–10% and 15% moisture content (Table 3). A high biomass moisture level significantly increased the *SER* of finer particle comminution of miscanthus and switchgrass. For example, to grind miscanthus with moisture content of 15% through 1 and 2 mm milling screen, the *SER* was approximately 50% higher than that of the size reduction of air dried biomass (7–10% of moisture content). However, it was reported that for a coarse milling screen, biomass moisture did not significantly affect breakdown *SER*. The *SER* to grind miscanthus and switchgrass with 15% of moisture content through 6 mm milling screen were similar to those of air dried biomass comminution (Miao et al., 2011). In comparing *SER* to grind grass and wood biomass, Schell and Harwood (1994) mentioned that straw and corn stover required 6–36% less energy for milling than wood; 222 kW h t^{-1} would be required to obtain a wood powder of 450 μm and below. Da silva et al. (2010) studied the effectiveness of wet disk milling (WDM) on treating sugarcane bagasse and straw. They reported that bagasse biomass was not easily grounded by WDM compared to straw, and each cycle lasted a long time. These steps increased significantly *SER* which reached 11,000 kW h t^{-1} for straw and 13,330 kW h t^{-1} for bagasse, to attain particle sizes which resulted in maximum cellulose conversion (Table 3). Fig. 4 represents and resumes the *SER*, as a function of screen size at moisture content of ~7–8%, for grinding selected lignocellulosic biomass using a hammer mill. The smaller the screen size, the higher the *SER*. Fig. 6 shows that wood biomass needed the highest specific energy to grind with all hammer mill screen sizes at ~7–8% moisture contents. In contrast, corn stover consumed lower energy compared to wheat and barley straw, switchgrass and wood biomass. Fig. 5 shows also the relationship between *SER* for biomass hammer milling at 7–8% and ~12% moisture content. The higher the moisture content, the higher the *SER*. It can be explained by the fact that an increase in moisture content of straw samples initially increases the shear strength of the material, although, thereafter shear strength rapidly decreases with decomposition of straw sample. The energy values required for size reduction of wheat straw, barley straw and switchgrass were much higher than that reported for reducing corn stover at the same moisture content and from the same initial size using the same hammer mill screen size. Corn stover used the least specific energy with hammer mill at 7–8% and 12% moisture content. This is in line with the expectation that corn stover would consume less energy due to its lower fiber content and the presence of more spongy vascular tissues in the stem (Mani et al., 2004). These results indicate clearly that the moisture content, physicochemical properties and tissues organization and composition of lignocellulosic substrates are very important parameters which can be considered in mechanical size reduction of lignocelluloses biomass. These comparisons suggest that the mechanical properties of lignocellulosic materials are dependent not only on the physicochemical characteristics and biochemical composition of the matrix but also on the tissues organization and composition.

5.2. Equipements and particle properties requirement of the final product

Specific energy requirement (*SER*) of size reduction of lignocellulosic biomass depends on the ratio of particle size distribution of materials before and after milling, which depend strongly on the equipements or machine used (Table 2). Studies have shown that particles sizes must be reduced to 0.5–2 mm to reduce heat and mass transfer limitation. This size reduction is not a cost-efficient process because it requires much energy. Hammer mills, knife mills, disk mills, ball mills, vibratory ball mills, colloid mills, cen-

Table 2
Specific energy requirement (*SER*) for mechanical size reduction of selected lignocellulosic biomass.

Biomasses	Equipment (size reduction)	Moisture content (% wet basis)	Initial size/screen size Size (mm)	Specific energy requirement (kW ht^{-1})	Ref.
Wheat straw	Hammer milling	12.1	7.7/3.2	24.7	Mani et al. (2004)
			7.7/1.6	43.6	Kratky and Jirout (2011)
		8.3	7.7[a]/3.2	11.4	
			7.7/1.6	37.0	
			7.7/0.8	51.6	
		4–7	22.4/3.2	21.0	
			22.4/1.6	42.0	
	Knife milling	4–7	22.4/2.5	6.4	
			22.4/1.6	7.5	
Barley straw	Hammer milling	6.9	20.5/3.2	13.8	Mani et al. (2004)
			20.5/1.6	37.9	
			20.5/0.8	53.0	
		12.0	20.5/1.6	27.1	
Corn stover	Hammer milling	12.0	12.5/1.6	19.8	Kratky and Jirout (2011)
		6.2	12.5/3.2	6.9	
			12.5/1.6	14.8	
			12.5/0.8	22.1	
		4–7	22.4/3.2	9.6.	
			22.4/1.6	14.0	
	Knife milling	4–7	22.4/6.3	15.0	
			22.4/3.2	20.0	
Switchgrass	Hammer milling	12.0	7.2/3.2	27.6	Mani et al. (2004)
			7.2/1.6	58.5	Bitra et al. (2009)
		8.0	7.2/3.2	23.5	Miao et al. (2011)
			7.2/1.6	51.8	
			7.2/0.8	62.6	
	Knife milling	ND	203/50	0.49	
			100/50	0.19	
		15	ND/1.0	378.0	
		15	ND/6.0	35.0	
		7–10	ND/1.0	230.0	
		7–10	ND/6.0	38.0	
Miscanthus	Knife milling	15	ND/1.0	394.0	Miao et al. (2011)
		15	ND/6.0	48.0	
		7–10	ND/1.0	250.0	
		7.10	ND/6.0	45.0	
Rice straw	Ball milling 5 min	4–6	ND/<2	2500.0	Hideno et al. (2009)
	Ball milling 30 min		ND/<2	15000.0	
	Ball milling 60 min		ND/<2	30000.0	
	Wet disk milling 9 min		ND/<2	250.0	
	Wet disk milling 30 min		ND/<2	1500.0	
Sugarcane straw	Wet disk milling 69 min		ND/<2	4111.0	Da Silva et al. (2010)
	Wet disk milling 123 min		ND/<2	7640.0	
	Wet disk milling 167 min		ND/<2	11000.0	
Bagasse	Wet disk milling 37 min		ND/<2	2940.0	
	Wet disk milling 82 min		ND/<2	6970.0	
	Wet disk milling 143 min		ND/<2	13333.0	
Hardwood	Hammer milling	6.0	19.1/1.6	130.0	Kratky and Jirout (2011)
		4–7	22.4/1.6	130.0	
			22.4/2.5	120.0	
	Knife milling	4–7	22.4/1.6	130.0	
			22.4/2.5	80.0	
	Wet disk milling	6.0	19.05/1.6	200–400	
	Vibratory ball milling	11	22.0/0.15	800.0	
Spruce chips	Wet disk milling	5.2	20–40/0.5	750.0	Zhu et al. (2010a,c)
		ND	8–22/1.8	460.0	Repellin et al. (2010)
	Centrifugal milling	ND	2–4/0.5	750.0	
Pine chips	Knife milling	6.7	1.5/0.71	237.7	Phanphanich and Mani (2011), Repellin et al. (2010)
Beech chips	Centrifugal milling	ND	2–4/0.5	850.0	Repellin et al. (2010)

trifugal mills, tumbling ball mills, planetary ball mills, jet mills, extruders, or innovative grinding processes can be used for mechanical size reduction of lignocellulosic biomass (Fig. 3). The choice of the right way of chipping, grinding and milling depends especially on the physicochemical properties of biomass, the final particle size, and moisture content (Adapa et al., 2010; Kratky and Jirout, 2011). For example, colloid mills and extruders are suitable only for comminuting wet materials with moisture contents above 15–25%, whereas hammer and knife mills are suitable only for comminuting dry biomass with moisture contents up to 10–15% (Kratky and Jirout, 2011). On the other hand, ball milling has been described as a “mechano-chemical” treatment, due to the effectiveness of prolonged milling on breaking chemical interactions between lignin and hemicelluloses, which would also in-

Table 3
Specific energy consumption for post-pretreatment size reduction of selected lignocellulosic biomass.

Biomasses	Physicochemical pretreatments	Equipment (size reduction)	Initial size/screen size Size (mm)	Specific energy requirement (kW ht^{-1})	Ref.
Wheat straw	Untreated	Hammer milling	30[a]/3.2	28.0	Adapa et al. (2010)
			30/1.6	42.6	
	Steam exploded	Hammer milling	30/3.2	14.7	
			30/1.6	22.9	
Barley straw	Untreated	Hammer milling	30/3.2	18.6	
			30/1.6	25.1	
	Steam exploded	Hammer milling	30/3.2	20.4	
			30/1.6	30.1	
Oat straw	Untreated	Hammer milling	30/3.2	29.6	
			30/1.6	41.5	
	Steam exploded	Hammer milling	30/3.2	19.5	
			30/1.6	33.2	
Pine chips	Untreated	Knife milling	~20/1.5	237.7	Phanphanich and Mani (2011), Repellin et al. (2010)
	Torrefied-225 °C	Knife milling	~20/1.5	102.6	
	Torrefied-250 °C	Knife milling	~20/1.5	71.4	
	Torrefied-275 °C	Knife milling	~20/1.5	52.0	
	Torrefied-300 °C	Knife milling	~20/1.5	23.9	
	Untreated	Wet disk milling	ND	616.0	Zhu et al. (2010a,b), Zhu and Pan. (2010)
	Hot water, 180 °C to 30 min (pH 5)	Wet disk milling	ND	537.0	
	H_2SO_4 2.2% w/w (pH 1.1)180 °C to 30 min)	Wet disk milling	ND	335.6	
	[b]SPORL (pH 4.2) 180 °C to 30 min)	Wet disk milling	ND	499.3	
	[b]SPORL (pH 1.9) 180 °C to 30 min)	Wet disk milling	ND	134.5	
Spruce chips	Untreated	Centrifugal milling	2–4/0.5	750.0	Repellin et al. (2010)
	Torrefied-240 °C	Centrifugal milling	2–4/0.5	206.0	
	Torrefied-280 °C	Centrifugal milling	2–4/0.5	126.0	
	134 °C, 2.4 bar	Wet disk milling	8–22/1.8	460.0	
	166 °C, 7.2 bar	Wet disk milling	ND	151.0	
	SPORL, 180 °C, 30 min	Wet disk milling	ND/1.02	124.0	
	SPORL, 180 °C, 30 min	Wet disk milling	ND/0.76	170.0	
Beech chips	Untreated	Centrifugal milling	2–4/0.5	850.0	
	Torrefied-240 °C	Centrifugal milling	2–4/0.5	162.0	
	Torrefied-280 °C	Centrifugal milling	2–4/0.5	98.5	

[a] Initial size (mm); ND: not determined; SPORL: sulfite pretreatment to overcome recalcitrance of lignocellulose.
[b] Sodium bisulfite charge was 8% on wood for two SPORL, H_2SO_4 charge was 2.2% (w/w) on OD wood for low pH (pH 1.9) and 0% for (pH 4.2).

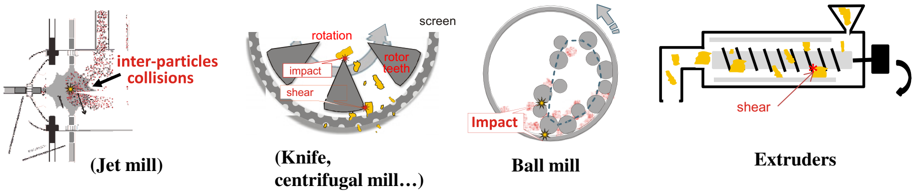

Fig. 3. Principle of mechanical size reduction and destructuring with different equipements.

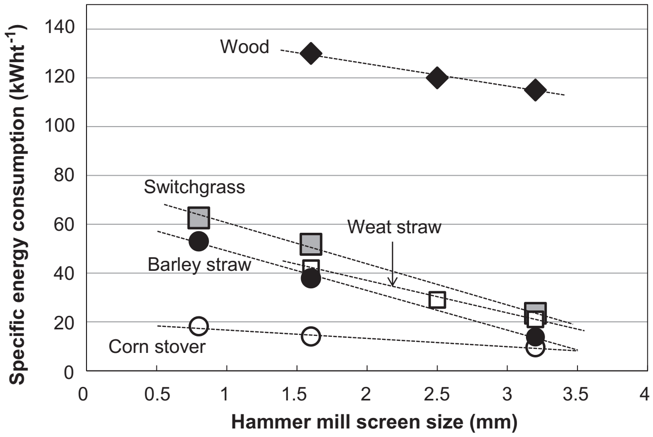

Fig. 4. Specific energy requirement (*SER*) for grinding selected biomass using hammer mills at ~7–8% moisture content.

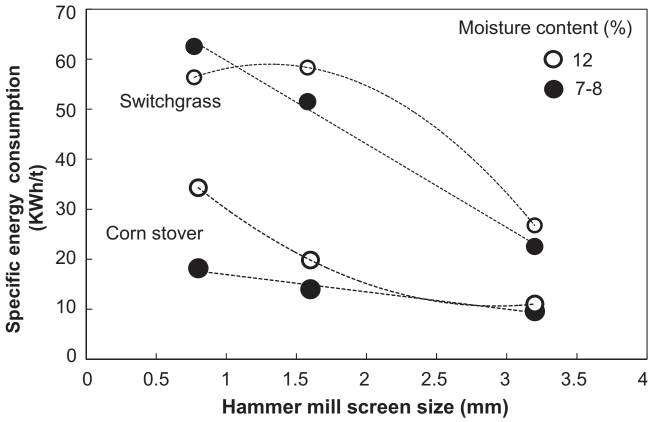

Fig. 5. Specific energy requirement (*SER*) for grinding of switchgrass and corn stover using hammer mills at ~12% and 7–8% moisture content.

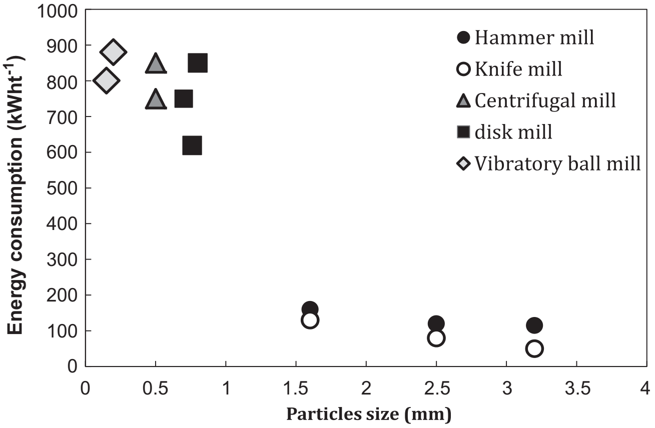

Fig. 6. Energy consumption of wood grinding as a function of final particle size in different pulverisation equipements.

crease enzymatic hydrolysis (Teramoto et al., 2008). Fluidized bed opposed jet mills have been widely used in various industrial fields for their excellent ability to improve the surface area and enhance the bioavailability by micronization, without sacrificing the natural physical-chemical properties of materials (Choi et al., 2001). Energy consumption for grinding wheat straw, corn stover and rice straw increases when screen opening size area changed from coarser to finer. Bitra et al. (2009) developed a knife mill based on linear shear action where switchgrass was shredded to particle sizes of 100 and 50 mm, respectively, (Table 2). The *SER* for disintegration of switchgrass from 203 to 100 mm and 50 mm was 0.49 and 0.19 kW h t^{-1}, respectively. In a comparison study, Cadoche and Lopez (1989) tested knife and hammer mills on hardwood chips and grass with moisture contents of 4–7%. The *SER* was 130 kW h t^{-1} with both hammer and knife mills to reduce hardwood chips and grass particles from 22.4 to 1.6 mm (Table 3). They reported that the hammer mill required more energy (120 kW h t^{-1}) than the knife mill (80 kW h t^{-1}) to achieve a final particle size of 2.5 mm for hardwood chips (Table 3). Shell and Harwood compared knife, hammer and disk millings of wood chips, wheat straw, and corn stover with moisture contents of 4–7%, to final particle size of 1.2 mm. They concluded that the disk mill had the highest *SER* with 200–400 kW h t^{-1}, followed by the hammer mill with 90–130 kW h t^{-1} and finally the knife mill with 80–120 kW h t^{-1}, all depending on the particle size (Table 2). Another study compared the energy consumption of hammer and disk milling and found that the *SER* to reduce hardwood from a particle size of 19.1–1.6 mm was 130 kW h t^{-1} with hammer mill and 200–400 kW h t^{-1} with disk milling (Kratky and Jirout, 2011). Even though vibratory ball milling treatments required 800 kW h t^{-1}, it allowed to reduce hardwood particle sizes from 22 mm to 150 µm, but centrifugal mill treatment required more energy for the pretreatment of both spruce and beech chips (Repellin et al., 2010). The energy consumption reached 750 kW h t^{-1} of spruce and 850 kW h t^{-1} of beech to reduce chips particles from 2–4 to 0.5 mm (Table 3). Fig. 6 summarizes the specific energy required (*SER*) by hammer, knife, centrifugal, disk and vibratory ball mills to grind hardwood and softwood lignocellulosic materials in relation to final particle size. From data presented in Table 3 and Fig. 6, it is seen that grinding energy increased greatly as the particle size decreased. Biomass over 1.5 mm screen size is usually comminuted by knife and hammer mills. Because of the energy requirement in relation to particle size, hammer and knife mills are the most commonly used machines in biomass size reduction technologies. The hammer and disk mills require more energy (~160 kW h t^{-1}) than the knife (~130 kW h t^{-1}) to achieve a final particle size of 1.6 mm for hardwood chips. However, it is difficult to reach final particle size of 0.5–1 mm using hammer and knife mills. Biomass with up to 0.1–1 mm screen size is comminuted by disk, centrifugal and vibratory ball mills. The *SER* in disc, centrifugal and vibratory ball milling process depends strongly on the time and cycle pass. If a disc mill is used, milling using more than one processing cycle is usually required. In general, there is no possibility to reach the final particle size in one pass through the mill. When fine particles are required, the energy demand in ball or disc milling is dramatically higher in comparison with other size reduction machines (see Fig. 6). Hideno et al. (2009) compared the *SER* of hot compressed water treatment (HCWT), wet disk milling (WDM) and dry ball milling (DBM) for rice straw disintegration to reach final particle sizes of <2 mm (initial particle size in not mentioned). They reported that the *SER* of the DBM increased proportionally with milling time and reached 30,000 kW h t^{-1} rice straw after 60 min (Table 2). Thus, the energy consumption of HCWT at 160 °C was 1583 kW h t^{-1} rice straw; 19 times lower than that of 60 min of DBM. These results indicate that the HCWT treatment is an economically efficient pretreatment of the enzymatic hydrolysis of rice straw. However, the HCWT generates toxic components, such as furfural and hydroxymethylfurfural (HMF) that have significant inhibitory effects on the metabolism of yeast, and are considered toxic to many organisms (Palmqvist and Hahn-Hägerdal, 2000). Combination of hot-compressed water treatment (HCWT) and wet disk milling (WDM) was investigated to improve the enzymatic digestibility of rice straw and enhance sugar recovery yield. Rice straw, cut to <3 mm, was autoclaved at 121, 135, and 150 °C for 60 min, and subsequently treated by wet disk milling. WDM with HCWT at 135 °C for 60 min produced maximum xylose and glucose yields of 79% and 90%, respectively, (Hideno et al., 2012). In contrast, the *SER* of WDM increased slightly with the number of operations cycles. It was 1500 kW h t^{-1} rice straw for 10 operations, which corresponded with maximum sugar yield. While DBM and HCWT are batch operations, WDM is a continuous process that is suitable for the mass treatment of lignocellulosic biomass. However, WDM treatment resulted in lower glucose yield and required more energy for the pretreatment of both bagasse and sugarcane straw (Da Silva et al., 2010). The *SER* reached 11,000 kW h t^{-1} of sugarcane straw and 13,333 kW h t^{-1} of bagasse, which resulted in maximum cellulose conversion (Table 2). These results suggest that WDM treatment is more sensitive to the type of biomass. Da Silva et al. (2010) reported that sugarcane straw and bagasse responded differently to BM and WDM pretreatments, as BM is more effective for bagasse, whereas WDM is more adequate for straw pretreatment. BM improved the enzymatic hydrolysis by decreasing cellulose crystallinity, while the defibrillation effect observed for WDM samples seems to have favored enzymatic conversion. BM is energy-intensive and at larger scale, it is an expensive treatment. WDM has been shown to be an economically reasonable pretreatment of rice straw, even though it did not result in attractive results with bagasse biomass. Thus, modifications of disk milling or combining with other pretreatments should help to break down this type of biomass. It is clear that pretreatment concern a "tailor-made" process for each individual material, and that the specific energy consumption can be affected by lignocellulosic material properties, moisture content, and screen size.

6. Coupling of chemical and physicochemical with mechanical pretreatments "post-pretreatments"

The mechanical size reduction is considered to be one of the most expensive processing steps in biorefinery in terms of energy and operating costs. Size reduction process has a high energy

Table 4
Energy efficiency of different pretreatment processes applied to selected lignocellulosic biomass.

Substrates	Treatment conditions		Total glucose recovery (g/kg biomass)	Total pretreatment energy (kW h/kg)	η (kg glucose kW h^{-1})	Ref.
Lodgepole pine		Wet disk milling	54.0	0.62	0.088	Zhu et al. (2010a,b)
	Hot water 180 °C, 30 min	Wet disk milling	160.0	0.54	0.298	
	H_2SO_4 180 °C, 30 min	Wet disk milling	157.0	0.34	0.469	
	SPORL pH 4.2	Wet disk milling	431.0	0.50	0.864	
	SPORL pH 1.9	Wet disk milling	382.0	0.14	2.830	
Spruce	Chopping 2-10 mm	Steam explosion 215 °C	346.0	0.55	0.629	Wingren et al.(2003)
Lodgepole pine	Chopping 2-10 mm	Organosolv 170 °C	347.0	0.45	0.771	Pan et al. (2008)
Eucalyptus	Hot water 180 °C	Wet disc milling 3 cycles	421.0	0.41	1.017	Lee et al. (2010b)
Oilseed rap straw	Hemmer milling	H_2SO_4 90 min, 130 °C	313.0	0.41	0.756	Mathew et al. (2011a,b)
	Hemmer milling	H_2SO_4 60 min, 130 °C	306.0	0.33	0.939	
	Hammer milling	NaOH 130 °C, 30 min	469.0	0.33	1.421	
Bagasse		Wet disc milling 10	135.0	2.94	0.046	Da Silva et al. (2010)
		Wet disc milling 20	213.0	6.97	0.031	
Sugarcane straw		Wet disc milling 10	208.0	7.60	0.027	
		Wet disc milling 20	245.0	11.00	0.022	
Rice straw		Ball milling 5 min	194.0	2.50	0.078	Hideno et al. (2009)
		Ball milling 15 min	245.0	7.50	0.033	
		Ball milling 60 min	331.0	30.00	0.011	
	Hot water 160 °C		260.0	1.60	0.163	
	Hot water 180 °C		312.0	1.83	0.170	
		Wet disc milling 1 cycles	174.0	0.08	2.096	
		Wet disc milling 3 cycles	184.0	0.25	0.736	
		Wet disc milling 10 cycles	292.0	1.50	0.195	

requirement and is not economically advantageous in general. The recommended particle size is <3 mm for effective accessibility and hydrolysis to lignocellulosic material. Thus, it is necessary to reduce biomass in size. To counteract these disadvantages, the size reduction can be combined with chemical and physicochemical pretreatments, in order to save energy at grinding and enzyme loading for biological and chemical accessibility and degradation. To reduce mechanical energy consumption for lignocellulosic biomass size reduction through milling/grinding, some works proposed an approach of combined physicochemical pretreatment (process 1, Fig1). The benefits in energy savings achieved using this combined physicochemical/size reduction pretreatment approach is significant, based on previous studies. Adapa et al. (2010) reported that energy consumption for agricultural biomass size reduction decreased significantly with steam exploded substrates. The specific energy required to grind steam exploded oat and wheat straws, using 3.2 and 1.6 mm hammer mill screen sizes, was 52% and 25%, and 90% and 64% lower than non-treated straws, respectively, (Table 4). On the other hand, the specific energy required to grind non-treated and steam exploded barley straw using 3.2 and 1.6 mm hammer mill screen sizes was not statistically different (Adapa et al., 2010). Steam exploded barely straw hammer milled with 3.2 and 1.6 mm screen sizes consumed 9% and 17% higher specific energy as a compared to non-treated barely straw (Table 3). During the steam explosion process, the organized lignocellulosic matrix disintegrated into finer components hence requiring lower specific energy for grinding purpose. The difference between barley and wheat/oat straws can be attributed to physicochemical characteristics (cellulose crystallinity, structure of hemicelluloses, lignin composition and content and cross linking, tissues organization, etc.), all of which depend on the species and plant parts. Another study investigated the influence of torrefaction, an oxygen-free mild thermal treatment, on wood grinding energy (Phanphanich and Mani, 2011; Repellin et al., 2010). They observed that the energy requirement to reduce pine, spruce and beech chips using knife mill and centrifugal mill was very high. Specific energy consumption for grinding was significantly reduced with increased torrefaction temperatures for pine, spruce and beech chips (Table 3). Grindability of torrefied pine chips was substantially improved after torrefaction at 275 and 300 °C as the specific energies required for grinding (24–52 kW h t^{-1}) were as low as that to grind grasses such as wheat straw, barley straw, corn stover and switchgrass using a similar sieve size of 1.6 mm (Table 4). In the case of beech and spruce chips, grinding energies decreased to values below 100 kW h t^{-1} at high temperature, while the energy consumption to grind non-torrefied spruce and beech chips was as high as 750 and 850 kW h t^{-1}, respectively, (Table 3). Compared to untreated wood chips samples, torrefaction at 300 °C reduced grinding energy consumption by 10 times for pine chips and by 4 and 8 times at 280 °C for spruce and beech chips, respectively. These results suggest that improved grindability of torrefied biomass may primarily be due to relative increase in biomass brittleness and breakdown of fibrous compounds due to thermal damages (Arias et al., 2008). Recently Zhu et al. (2009) studied the effects of chemical pretreatments and disk-milling conditions on energy consumption for size-reduction of softwood. They found that combined chemical-size-reduction pretreatments of forest biomass can lower grinding energy consumption by 20–80%, depending on the pretreatment applied under conditions corresponding to 20% solids-loading and a disk-plate gap of 0.76 mm in milling. SPORL (Sulfite Pretreatment to Overcome Recalcitrance of Lignocellulose) is a mild pretreatment conducted at a temperature between 160 and 190 °C for a period of 10–30 min in a batch mode. It was reported that SPORL pretreatment before size reduction significantly reduced energy consumption by an order of magnitude. With a treatment at 134 °C, 2.4 bars, the energy consumption of ball milling to reduce spruce chips from 8–22 to 1.8 mm was 460 kW h t^{-1} (Table 4). SPORL with a sodium bisulfite charge of 8% and sulfuric acid charge of 2.21% on wood was the most effective in decreasing size-reduction energy consumption. SPORL pretreatment at 180 °C during disk milling was sufficient to obtain almost complete cellulose digestibility, and the energy consumption for this was only 124 kW h t^{-1}. Solids-loading had the most significant effect on disk-milling energy. When solids-loading was reduced from 30% to 3%, disk-milling energy could be decreased by more than a factor 10 for wood chips pretreated by both SPORL and dilute-acid at an acid charge of 2.21%. Similar effects on size-reduction energy savings and excellent enzymatic hydrolysis yields were also achieved when large disk-plate gaps (up to 1.52 mm) were applied in disk-milling of wood chips pretreated by SPORL together with acid (Zhu et al., 2009, 2010a). The coupling of mechanical size reduction with chemical and physicochemical pretreatments strongly suggest that the digestibility is substantially improved and to reduce significantly the energy requirement while preserving lignocellulosic polymers. This would improve the whole process economics. These data indicate clearly that combined pretreatments are very important for the reduction of the energy consumption in dry plants biorefinery. It should be noted that the total energy consumption also includes thermal energy used for thermochemical pretreatment conducted at elevated temperatures. The thermal energy depends on two factors: (i) liquid (water)-to-biomass ratio (L/B) and (ii) pretreatment temperature (Zhu et al., 2010a, 2009). The thermal energy consumption for pretreatment is almost linearly proportional to liquid/biomass ratio; thus, reducing liquid/biomass ratio is very much needed in order to improve energy efficiency. This poses a significant opportunity for physicochemical and -biological "solid state" pretreatments combined with size reduction, because the liquid/biomass ratio is very low in this case; moreover, physicochemical and -biological "solid state" pretreatment coupled to physical treatment (size reduction) may be used directly in a downstream process without washing, drying and pH adjustments.

7. Energy efficiency in mechanical size reduction of lignocellulosic biomass with respect to glucose yields

The pretreatment energy efficiency (kg glucose extracted kW h^{-1}) was calculated according to Zhu et al. (2010a). The amount of glucose recovered after enzymatic hydrolysis (g glucose/kg biomass) was divided by the total energy consumed for pretreatment (kW h kg^{-1} biomass: Eq. (1). The total energy consumed during the fractionation process is defined as the sum of energy required for milling and chemical or physicochemical pretreatment.

$$\eta_{\text{pretreatment}} = \frac{\text{Total glucose yield (g glucose kg}^{-1}\text{ biomass)}}{\text{Total energy consumed (KW h kg}^{-1}\text{)}} \qquad (1)$$

The present definition is independent on the lignocellulosic carbohydrates content by normalizing the total sugar yield using the sugar content in the feedstock. A simple energy balance calculation reveals energy consumption for lignocellulosic biomass-size reduction. Both total sugar recovery and pretreatment energy efficiency should be used in evaluating and comparing the performance of pretreatment processes (Wyman et al., 2009). The effect of pretreatment time on energy efficiency was evaluated to identify the optimum pre-treatment conditions in terms of amount of sugar extracted per kW h energy consumed. This is important to establish the net energy output in bioethanol and biogas production from lignocellulosic biomass. However, literature concerning the energy consumption and energy efficiency of chemical, physicochemical and mechanical treatment is scarce. Indeed, it is very difficult to carry out an in-depth comparison, because most published studies on the pretreatment processes were conducted under a wide variety of conditions in different laboratories around the world. A global harmonization initiative is needed. Table 4 presents the details of energy efficiency (η) of different pretreatments from previous studies. After combined physicochemical/mechanical size reduction of lodgepole pine wood, the highest glucose yield (413 g/kg biomass) was obtained from SPORL-pretreated biomass at pH 4. However, the highest η obtained was 2.83 kg glucose kW h^{-1}, for lodgepole pine biomass pretreated with 2.2% H_2SO_4 (w/w) (pH 1.9) for 30 min at 180 °C followed by disk milling (Zhu et al., 2010a, 2009). The mechanical energy required for milling was 50 kW h t^{-1} of wood. Disk milling without physicochemical co-treatment consumed the highest amount of energy; as a result the disk milling results showed the lowest η obtained, being 0.088 kg glucose kW h^{-1}. The SPORL disk milling approach significantly reduced total energy consumption with excellent sugar recovery. With regards to organosolv pretreatment of lodgepole pine biomass, the highest glucose yield was obtained from biomass pretreated at 180 °C. Furthermore, the thermal energy consumption for aqueous organosolv pretreatment at 170 °C is about 6% lower than that at 180 °C. Consequently, the highest η obtained was 0.77 kg glucose kW h^{-1} from biomass pretreated at 170 °C (Pan et al., 2008; Zhu et al, 2010a). According to Wingren et al. (2003), the η of steam exploded spruce wood biomass at 215 °C was 0.63 kg glucose kW h^{-1}. The spruce wood milling energy demand was 50 kW h t^{-1} of wood. However, the η of hot water (180 °C) disk milling of eucalyptus wood was 1.02 kg glucose kW h^{-1}. Energy consumption by steam explosion is largely attributed to latent heat with a minor effect of the final steam explosion temperature. Therefore, only one temperature of 215 °C used in the study of Wingren et al. (2003) was used in the calculation. On the other hand, an L/B ratio has a significant effect on thermal energy consumption for aqueous organosolv pretreatments. At the end published data (Table 4) show that combined SPORL (pH 1.9) and hot water (180 °C) disk milling produced the highest sugar yield from wood biomass among all five processes. Steam explosion and disk milling consumed the highest amount of energy. As a result, steam explosion and disk milling without co-treatment have the lowest η i.e., 0.63 and 0.088 kg glucose kW h^{-1}, respectively. SPORL/mechanical treatment process was better in energy efficiency (η) compared to steam explosion and organosolv processes. According to the studies of Mathew et al. (2011a,b), energy efficiency of acid and alkaline pre-treatment of oilseed rap (OSR) straw was evaluated (Table 4). The maximum sugar extracted after acid pre-treatment and hydrolysis was obtained from biomass pretreated for 90 min (Mathew et al., 2011a). However the η was found to be lower when biomass had been pre-treated for 90 min than for 60 min. Hence, it is concluded that the highest η obtained was 0.94 kg glucose kW h^{-1} from a pre-treatment time of 60 min. However, during alkaline pretreatment, the highest glucose yield 462 g glucose kg^{-1} biomass was obtained from biomass pretreated for 30 min at 0.63 mol/dm^3 NaOH concentration (Mathew et al., 2011b). The highest η obtained after alkaline pretreatment was 1.42 kg glucose kW h^{-1} from biomass pretreated for 30 min at 130 °C and a NaOH concentration of 0.63 and 0.75 mol/dm^3. The authors have shown that a higher concentration of glucose can be extracted from OSR straw per kW h of energy consumed when alkaline pretreatment was used in contrast to acid pretreatment. They have concluded that alkaline pretreatments are more efficient than acid pretreatments in terms of glucose and energy efficiency. Da Silva et al. (2010) studied the efficiency of wet disk milling (WDM) on bagasse and sugarcane straw for bioethanol production. According to data presented in Table 4, for experiments carried out using WDM, the enzymatic hydrolysis yields increased with the number of cycles, and maximum sugar yields were obtained after 20 cycles for both bagasse and straw, which yielded 213 and 245 g glucose kg^{-1} biomass, respectively. However, the highest η obtained was 0.046 and 0.027 kg glucose kW h^{-1}, for bagasse and straw biomass, respectively, after only 10 cycles WDM while 20 cycles consumed the highest amount of energy, corresponding to the lowest η. WDM was more effective for bagasse than for straw. The effects of WDM treatment were then more sensitive on the type of material. Hideno et al. (2009) reported promising data for the

Table 5
Effect of pretreatments on structural features of lignocellulosic biomass and relationship with bioconversion.

Pretreatments	Mechanical size reduction		Physicochemical	Physicochemical pretreatment coupled to mechanical size reduction	"Solid state" physicochemical or biological pretreatment coupled to mechanical size reduction (proposed in this review)
Structural features	Ball, vibratory and disk milling	Hammer and knife milling	(Steam explosion, organosolv. acid, alkaline, oxidation, etc)		
Particle size	●●●●	●●	○		
Porosity	●●	●●	●●		
Specific surface area	●●●●	●●	●		
Degree of polymerization	●	●	●●●		
Crystallinity	●●●●	●●	○		
Holocelluloses solubilization	○	○	●●		
Holocelluloses recovery (%)	100	100	40–70	40–70	100
Energy consumption	++++	+++	+	++	+
Environmental toxicity	○	○	+++	+++	–
Bioconversion	++	+	++	++++	++++

●●●● Major positive effect; ● minor positive effect; ○ no effect.
+High/−low.

hydrolysis of WDM treated rice straw (Table 4), which reached 292 g glucose kg^{-1} biomass after 10 operation cycles, with an energy consumption of 1.5 kW h/kg of rice straw. However, in terms of energy efficiency a WDM pretreatment of one operation cycle appeared more preferred than 10 cycles. But in terms of energy efficiency, a WDM pretreatment of one cycle is more preferable than HCWT at 180 °C. WDM process was better from energy efficiency (η) compared to both HCWT and BM process. Moreover, WDM may be used directly in biorefineries without washing, separation, chemical and pH adjustments. The highest η obtained was 2.096 kg glucose kW h^{-1}, for rice straw after one cycle. This study demonstrated that WDM-1 cycle is comparable to SPORL (2.8 kg glucose kW h^{-1}), and more effective than steam explosion (0.629 kg glucose kW h^{-1}) and organosolv (0.771 kg glucose kW h^{-1}) processes. Additionally, WDM was more effective for rice straw than for bagasse and sugarcane straw. Hideno et al. (2009) compared the efficiency energy of ball milling (BM), WDM and HCWT. In BM, the monomeric sugar yields after enzymatic hydrolysis increased with milling time (Table 4). They suggested that the optimal milling time was 60 min with the highest yield of glucose (331 g glucose kg^{-1} rice straw). However BM treatment at 60 min resulted in lower η compared to DM-5 min and -10 min for the pretreatment of rice straw. The highest η obtained was 0.078 kg glucose kW h^{-1}, for rice straw after BM at 5 min. The HCWT of rice straw were performed at 160 and 180 °C. Both HCWT treatments were effective for enzymatic hydrolysis. The glucose yield after enzymatic hydrolysis at 180 °C was 313 g glucose kg^{-1} rice straw, higher than that at 160 °C and higher than WDM treatment for one cycle (Table 5). From the discussions above, physicochemical treatments combined with size reduction processes appear to represent the most promising technologies for improving lignocellulosic biomass bioconversions. On other hand, it is imperative to consider the energy requirements together with sugar yield for the evaluation of any pretreatment process.

8. Conclusions

Mechanical size reduction was found to be effective in decreasing particle size; decreasing cellulose crystallinity; increasing total accessible specific surface area; increasing pore size of particles; separating the main botanical parts of the crop into different fractions, to be used as feedstock for various applications. However, mechanical size reduction also has disadvantages. Milling has a high energy requirement and is not economically feasible in general compared to others pretreatment (Table 5). The performance and the energy requirement of mechanical size reduction of lignocellulosic biomass mainly depend on the ratio of particle size distribution of materials before and after milling; the moisture content; the lignocellulosic proprieties and the machine type and parameters (feed speed, cutting speed, geometry, etc.). The optimization of these parameters and/or the combinations of mechanical size reduction with others pretreatment can save energy and enzyme loading for enzymatic hydrolysis.

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